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Dynamic mechanical analysis of high pressure polymerized urethane dimethacrylate

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ABSTRACT

Objectives. The aim of this study was to compare the viscoelastic properties of high pressure (HP) polymerized urethane dimethacrylate (UDMA) with those of control, ambient pressure thermo-polymerized and photo-polymerized, UDMA and to assess the effect of varying polymerization parameters (protocol, temperature, and initiator) on the viscoelastic properties of HP polymerized UDMA.

Methods. The viscoelastic properties of the two control polymers, polymerized under atmospheric pressure, and four experimental polymers, polymerized under HP, were determined via dynamic mechanical analysis (DMA), in three point bending configuration. Atomic force microscopy (AFM) was used to characterize fractured polymer surface morphologies.

Results. The results showed that: HP-polymerization lead to a polymer with significantly higher T_g and E'_{rub}, indicative of a higher crosslink density; modifying the polymerization protocol resulted in a significant increase in $\tan\delta$; increasing the polymerization temperature lead to a significant decrease in E'_{rub} and T_g; and that the polymer with no initiator had the lowest E', E'', T_g, and E'_{rub} and the highest $\tan\delta$, suggesting that under this conditions a polymer with significantly reduced crosslink density had been obtained. A characteristic nodular appearance was seen for the two control polymers under AFM, while a modified surface morphology was present in the case of HP polymerized materials.

Significance. The DMA results suggest that polymerization under HP resulted in polymers with an increased crosslink density and that the higher polymerization temperature or the lack of initiator was detrimental to the viscoelastic properties determined. Changes in polymer network morphology were identified by AFM characterization.

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1. Introduction

The fabrication of crowns and fixed partial dentures (FPDs) using dental computer aided design/computer aided machining (CAD/CAM) systems is nowadays current practice due to the standardization and the efficiency of the manufacturing process [1,2]. Esthetic appearance is quintessential in modern clinical practice and lead to an explosion in available cosmetic materials. Biocompatibility, good mechanical and excellent esthetic properties have rendered dental ceramics as a first choice among them. However, their manufacturing through milling is difficult and intraoral repair remains a challenge. Dental resin composites offer a viable alternative approach and several CAD/CAM composite blocks are currently available on the market. Their attractiveness lies in good esthetic properties, significantly easier machinability, and, purportedly, easier repair. Their mechanical properties have been improved by optimizing the fillers, the filler volume fraction, and their integration into the matrix by coupling agents [3,4]. However, poor long term stability, poor fatigue performance, loss of esthetic properties are mainly due to the organic phase. Thus, the lack of chemical stability of polymers coupled with their water sorption properties result in deterioration of optical properties of resin composites. Moreover, the release of unpolymerized monomers, which increases in an inverse proportional manner with the degree of conversion (DC) [5], and/or degradation products leads to biocompatibility concerns. Dental resin composites matrix is generally composed of a mixture of high molecular weight dimethacrylate monomers (such as bisphenol A glycidyl methacrylate – Bis-GMA and urethane dimethacrylate – UDMA) and lower molecular weight monomers (such as triethyleneglycol dimethacrylate – TEGDMA), which are used in order to reduce viscosity and facilitate the incorporation of fillers [6,7]. It has been demonstrated that low molecular weight monomers are more toxic to pulpal cells [8] and are released at higher rates than high molecular weight ones [9]. Among the high molecular weight monomers, UDMA, a monomer with a highly flexible structure, has been gaining attention since it is the least sensitive to release [9,10] and it does not contain bisphenol A, a substance which is widely discussed due to potential health related issues [11,12].

Studies on mechanical properties of resin composites have established that UDMA-based materials had superior flexural strength, in the 140 MPa range [13], compared to that Bis-GMA-based materials, in the 86 MPa [14] to 110 MPa [13] range. Even if the individual contribution of a specific component (matrix, filler, or coupling agent) to the properties of a composite is difficult to assess, it has been established that matrix properties influence the thermo-mechanical properties of dental resin composites [15,16], which are strongly linked to their mechanical properties [13,17,18]. Viscoelastic properties of UDMA/TEGDMA copolymers [19], as well as those of other copolymers [20–23] have already been studied and characterized. However, as far as these authors are aware, the characterization a pure UDMA-based matrix has not been reported.

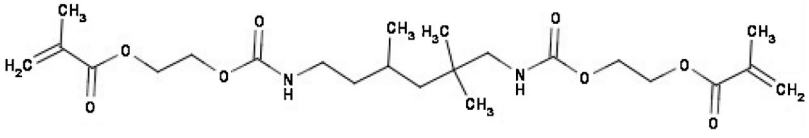
Thermo-polymerization is currently the most common method of fabrication of CAD/CAM composite blocks. Shrinkage induced during thermo-polymerization leads to the presence of defects and high internal stress [24]. A possible alternative, which could minimize this, is high pressure (HP) polymerization. It has been shown that polymerization under HP limits internal stress by reducing free volume [25,26]. Furthermore, it has been reported that HP polymerization increases the density and elastic modulus of polymers [27,28] and leads to dental composites with improved mechanical properties [29].

The aims of this study were: to compare the viscoelastic properties of HP polymerized UDMA with those of both ambient pressure thermo-polymerized and photo-polymerized UDMA and to assess the effect of varying polymerization parameters (protocol, temperature, and initiator) on the viscoelastic properties of HP polymerized UDMA; to assess the effect of the different polymerization protocols on the surface morphology of the polymers using atomic force microscopy (AFM). The null hypotheses tested were: (1) there is no difference in viscoelastic properties between ambient pressure polymerized and HP polymerized UDMA; (2) polymerization protocol does not influence the viscoelastic properties of HP polymerized UDMA; (3) polymerization temperature does not influence the viscoelastic properties of HP polymerized UDMA; (4) the initiator does not influence the viscoelastic properties of HP polymerized UDMA; (5) there is no difference in the surface morphology of the different polymers at the AFM level.

2. Materials and methods

2.1. Polymers

The UDMA monomer used in this study was 7,7,9(Or 7,9,9)-trimethyl-4,13-dioxo-3,14-dioxa-5,12-diazahexadecane-1,16-diyl bismethacrylate (MW = 470.56; CAS 72869-86-4; Esstech, Essington, USA):



For all the experimental groups, polymerization under HP was achieved by placing ~100 g monomer into a silicone tube (25 mm internal diameter, 1 mm thickness) that was then introduced into a custom-built autoclave with pressure and temperature control (LabVIEW version 8.2, National Instruments, USA) [29]. A thermocouple was placed in the proximity of samples to enable accurate monitoring and, via feed-back, control of the temperature. In the first stage, the pressure within the autoclave was increased from 0.1 MPa to 300 MPa at a rate of 0.1 MPa/s at ambient temperature. In the second stage, the temperature was increased to the desired temperature at